

## PATENT ABSTRACTS OF JAPAN

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## (54) ADHERENT COVER FILM

## (57)Abstract:

PROBLEM TO BE SOLVED: To prepare an adherent cover film which has an excellent fine-processability and comprises a polyimide film and a polyimide-based adhesive that develop sufficient heat resistance and adhesive properties.

SOLUTION: This adherent cover film has a constitution of laminating a 0.5-5  $\mu\text{m}$  bonding layer on a high-modulus very thin polyimide film which has a thickness of 10  $\mu\text{m}$  or less, preferably 3-7.5  $\mu\text{m}$  and contains no inorganic filler, and realizes a fine-processability that has never been experienced by making the total thickness 10  $\mu\text{m}$  or less. Further, by constituting the bonding layer being with a soluble thermoplastic polyimide resin, an epoxy resin and a curing agent thereof, the cover film develops excellent electric reliability, adhesive properties and heat resistance.

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## CLAIMS

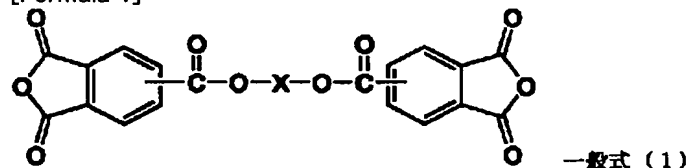
## [Claim(s)]

[Claim 1] The adhesive covering film whose total thickness it is 10 micrometers or less, and it has the configuration which carries out the laminating of the adhesives containing solvent fusibility thermoplasticity polyimide, an epoxy resin, and a curing agent to at least one side of the thin polyimide film whose fine particles with a mean particle diameter of 1 micrometers or more are two or less [ 100 //mm ] by the thickness of 0.5-5 micrometers, and is 10 micrometers or less.

[Claim 2] The adhesive covering film whose total thickness it is 3-7.5 micrometers, and it has the configuration which carries out the laminating of the adhesives with which fine particles with a mean particle diameter of 1 micrometers or more become at least one side of the thin polyimide film which is two or less [ 100 //mm ] from solvent fusibility thermoplasticity polyimide, an epoxy resin, and a curing agent by the thickness of 0.5-5 micrometers, and is 10 micrometers or less.

[Claim 3] More than 50 mol % of the acid 2 anhydride residue which the glass transition temperature of said solvent fusibility thermoplasticity polyimide is 200 degrees C or less, and is contained in this solvent fusibility thermoplasticity polyimide is a general formula (1).

## [Formula 1]

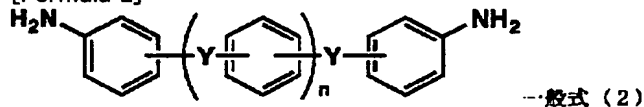


(式中、Xは $-(CH_2)_k-$ 、または芳香環を含む二価の基を示し、kは1以上10以下の整数である。)

The adhesive covering film according to claim 1 or 2 which comes out and is characterized by being the ester acid 2 anhydride residue expressed.

[Claim 4] More than 50 mol % of the diamine residue by which said solvent fusibility thermoplasticity polyimide is contained in this polyimide is the following general formula (2).

## [Formula 2]



(式中、Yは $-C(=O)-$ 、 $-SO_2-$ 、 $-O-$ 、 $-S-$ 、 $-(CH_2)_m-$ 、 $-NHCO-$ 、 $-C(CH_3)_2-$ 、 $-C(CF_3)_2-$ 、 $-C(=O)O-$ 、または単結合を示す。  
mおよびnは1以上5以下の整数である。)

An adhesive covering film given in any 1 term of claims 1-3 which come out and are characterized by being the residue of a diamine compound expressed.

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the thin adhesive property film with which micro processing is called for. Furthermore, it is related with an adhesive covering film useful in the field as which micro-processing nature, such as a tape for a flexible printed circuit board and TAB (Tape Automated bonding), a compound leadframe, a charge of a laminated wood, and electronic parts, thermal resistance, and an adhesive property are required in detail.

[0002]

[Description of the Prior Art] In recent years, advanced features of electronic equipment, high-performance-izing, and a miniaturization are progressing, and the miniaturization to the electronic parts used in connection with them and lightweight-ization have been called for. Therefore, high density and what is highly efficient and highly efficient have come to be called for more also for the wiring material or wiring components which mount the semiconductor device package approach and them. The covering film material which can be used especially suitable for printed wired board ingredients, such as high-density-assembly ingredients, such as a semiconductor package, COL and a LOC package, and MCM (Multi Chip Module), and Multilayer FPC, and in which an adhesive property possible [ micro processing ] and good is shown is called for. However, as for the covering film material conventionally used in these fields, the thing with a thickness of 50 micrometers or more was used from the field of adhesion dependability and electric dependability. If an aspect ratio is large, since it will be hard to process it, the adhesive covering film with the thick thickness of 10 micrometers or more does not fit the application asked for micro processing 5 micrometers or less. Moreover, in this field, the adhesive film which carried out the laminating of the adhesives of a phenol system and an epoxy system and the acrylic adhesives to one side or both sides of a polyimide film until now was used, a glue line — from the point of dependability, such as thermal resistance and an electrical property, — since polyimide system adhesives are used gradually.

[0003] Since it excels in thermal resistance also in various organic polymers, to space and the aeronautical-navigation field, polyimide is used broadly and used also as a charge of a binder. However, heat-resistant high polyimide system adhesives require the elevated temperature around 300 degrees C, and the high-pressure force, in order to paste up, and adhesive strength cannot say them with it being so high, either.

[0004]

[Problem(s) to be Solved by the Invention] Then, this invention persons came to complete this invention, as a result of micro processing's inquiring wholeheartedly for the purpose of offering an easy adhesive covering film, having solved the above-mentioned technical problem and maintaining thermal resistance and an adhesive property.

[0005]

[Means for Solving the Problem] This invention offers the new adhesive covering film which has the following configurations, and, thereby, the above-mentioned purpose is attained.

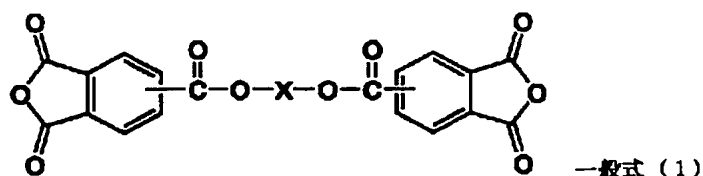
1) The adhesive covering film whose total thickness it is 10 or less micrometers, and it has the configuration which carries out the laminating of the adhesives containing solvent fusibility thermoplasticity polyimide, an epoxy resin, and a curing agent to at least one side of the thin polyimide film whose fine particles with a mean particle diameter of 1 micrometers or more are two or less [ 100 //mm ] by the thickness of 0.5-5 micrometers, and is 10 micrometers or less.

2) The adhesive covering film whose total thickness it is 3-7.5 micrometers, and it has the configuration which carries out the laminating of the adhesives with which fine particles with a mean particle diameter of 1 micrometers or more become at least one side of the thin polyimide film which is two or less [ 100 //mm ] from solvent fusibility thermoplasticity polyimide, an epoxy resin, and a curing agent by the thickness of 0.5-5 micrometers, and is 10 micrometers or less.

3) More than 50 mol % of the acid anhydride residue which the glass transition temperature of said solvent fusibility thermoplasticity polyimide is 200 degrees C or less, and is contained in this solvent fusibility thermoplasticity polyimide is a general formula (1).

[0006]

[Formula 3]



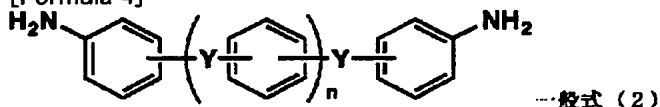
(式中、Xは $-(CH_2)_k-$ 、または芳香環を含む二価の基を示し、kは1以上10以下の整数である。)

An adhesive covering film given in 1 or 2 which comes out and is characterized by being the ester acid 2 anhydride residue expressed.

4) More than 50 mol % of the diamine residue by which said solvent fusibility thermoplasticity polyimide is contained in this polyimide is the following general formula (2).

[0007]

[Formula 4]



(式中、Yは $-C(=O)-$ 、 $-SO_2-$ 、 $-O-$ 、 $-S-$ 、 $-(CH_2)_m-$ 、 $-NHCO-$ 、 $-C(CH_3)_2-$ 、 $-C(CF_3)_2-$ 、 $-C(=O)O-$ 、または単結合を示す。  
mおよびnは1以上5以下の整数である。)

An adhesive covering film given in any 1 term of 1-3 which come out and are characterized by being the residue of a diamine compound expressed.

[0008]

[Embodiment of the Invention] The adhesive covering film of this invention carries out the laminating of the adhesives which become at least one side of a polyimide film from solvent fusibility thermoplasticity polyimide, an epoxy resin, and a curing agent, and is obtained. It is required to be less than [ polyimide film 10micrometer ] to be used. The thinner one of micro-processing nature is desirable, and since the thicker one of handling nature is desirable, its 3-7.5 micrometers are still more desirable [ nature ]. The film of an elastic modulus 2 or more [ 600kg //mm ] and beyond elongation-percentage 5% is [ a polyimide film ] still more desirable. It will be dealt with if an elastic modulus is low, difficulty is in a sex, and when an elongation percentage is low, there is a possibility of fracturing at the time of processing. Although polyimide usually contains fine particles, such as an inorganic filler, since it is in the inclination which stops being able to carry out easily for micro processing when using for the adhesive covering film of this invention, and a lot of fine particles more than mean particle diameter exist, it is desirable to use the polyimide film whose fine particles with a particle size of 1 micrometers or more are two or less [ 100 //mm ]. The number of the fine particles which exist in a film can be checked under a transparency mold microscope. Moreover, an adhesives layer has desirable 0.5-5 micrometers, and its 1-5 micrometers are still more desirable from an adhesive field. In this invention, it is important to set the total thickness after carrying out the laminating of the adhesives to a thin polyimide film to 10 micrometers or less. It is inferior to micro-processing nature in it being more than it. The adhesives used for the adhesive covering film of this invention contain solvent fusibility thermoplasticity polyimide, an epoxy resin, and a curing agent. After dissolving each adhesives constituent in an organic solvent, obtaining an adhesives solution and carrying out the cast to the shape of a film of a mold-releasing characteristic, these adhesives carry out heating removal, exfoliate from a mold-releasing film, may stick an organic solvent on a polyimide film, and even if they apply an adhesives solution to a direct polyimide film, remove a solvent and obtain the adhesive target covering film, they are not cared about. Although it dissolves solvent fusibility thermoplasticity polyimide, an epoxy resin, and a curing agent in an organic solvent and is obtained, since an adhesives solution can carry out desiccation removal of the solvent at low temperature comparatively, it is desirable to use the organic solvent containing a cyclic ether system solvent. As a cyclic ether system solvent, a tetrahydrofuran (THF), 1,4-dioxane, and dioxolane may be used preferably. Moreover, although it is more desirable to combine with a polar organic solvent when using the mixed organic solvent which mixed two or more solvents, the effectiveness of this invention tends to discover [ the way contained 50% of the weight or more preferably ] a cyclic ether system solvent 30% of the weight or more. In addition, as an organic polar solvent combined with a cyclic ether system solvent, acetamide system solvents, such as formamide system solvents [ , such as sulfoxide system solvents /, such as dimethyl sulfoxide and diethyl sulfoxide, /, N,N-dimethylformamide, N, and N-diethylformamide, ], N,N-dimethylacetamide, N, and N-diethylacetamide, are mentioned.

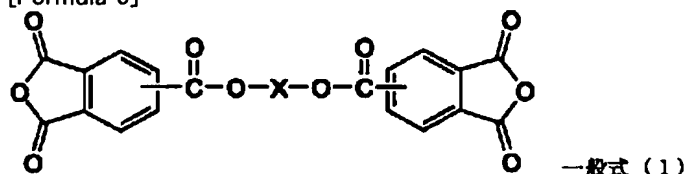
[0009] The solvent fusibility polyimide of this invention says what is dissolved in solvent dioxolane 10% or more at 25 degrees C.

[0010] More than 50 mol % of the acid 2 anhydride residue by which the solvent fusibility thermoplasticity polyimide of this invention is contained in a molecule although almost all thermoplastic polyimide is insoluble or refractory to these

solvents is a general formula (1).

[0011]

[Formula 5]

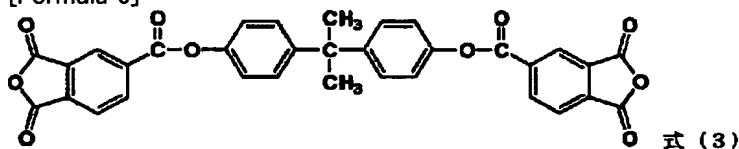


(式中、Xは $-(CH_2)_k-$ 、または芳香環を含む二価の基を示し、kは1以上10以下の整数である。)

Since it comes out and is characterized by being the ester acid 2 anhydride residue expressed, it can dissolve also in these organic solvents. As a desirable example of acid 2 anhydride expressed with a general formula (1) 2 and 2-screw (4-hydroxyphenyl) PUROPANJIBENZOETO -3, 3', 4, 4'-tetracarboxylic dianhydride, A p-phenylene screw (trimellitic acid monoester anhydride), 4, and 4'-biphenylene screw (trimellitic acid monoester anhydride), 1, 4-naphthalene screw (trimellitic acid monoester anhydride), 1, 2-ethylene screw (trimellitic acid monoester anhydride), 1, 3-trimethylene screw (trimellitic acid monoester anhydride), It is a formula (3) although 1, 4-tetra-methylenebis (trimellitic acid monoester anhydride), 1, 5-pentamethylene screw (trimellitic acid monoester anhydride), 1, and 6-hexa methylenebis (trimellitic acid monoester anhydride) etc. is mentioned.

[0012]

[Formula 6]

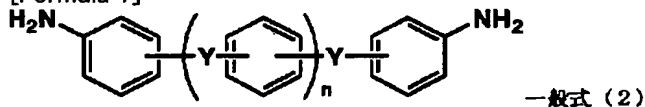


It comes out and 2 expressed, 2-screw (4-hydroxyphenyl) PUROPANJIBENZOETO -3, 3', 4, and especially 4'-tetracarboxylic dianhydride are desirable.

[0013] Moreover, as the acid 2 above-mentioned anhydride and a diamine component made to react, it is the following general formula (2).

[0014]

[Formula 7]



(式中、Yは $-C(=O)-$ 、 $-SO_2-$ 、 $-O-$ 、 $-S-$ 、 $-(CH_2)_m-$ 、 $-NHCO-$ 、 $-C(CH_3)_2-$ 、 $-C(CF_3)_2-$ 、 $-C(=O)O-$ 、または単結合を示す。  
mおよびnは1以上5以下の整数である。)

It comes out and the diamine compound expressed, especially screw (amino phenoxyphenyl) sulfone are desirable. In addition, in a general formula (2), you may differ, even if two or more Y is the same between each repeat unit, and the hydrogen of each benzene ring may be suitably permuted by substituents various by within the limits which this contractor can consider. For example, although halogen radicals, such as hydrocarbon groups, such as a methyl group and an ethyl group, and Br, Cl, can be mentioned, it is not limited to these substituents. Furthermore, among the diamine compound expressed with a general formula (2), since the diamine compound which has an amino group in the meta position has the good solubility to the organic solvent of the thermoplastic polyimide which used it, the adhesives solution excellent in workability is obtained and it is desirable. In addition, two or more sorts may be mixed and used for the diamine compound expressed with a general formula (2).

[0015] The thermoplastic polyimide which dissolves in the polyimide system adhesives solution of this invention carries out the dehydration ring closure of the polyamide acid polymer which is the precursor, and is obtained. this polyamide acid solution — said acid 2 anhydride carried out and said diamine compound carried out — substantial — etc. — it is used so that it may become a mol, and in an organic polar solvent, a polymerization is carried out and it is obtained.

[0016] This polyamide acid or polyimide is obtained from the polyamide acid polymer which sets in the inert atmosphere of an argon, nitrogen, etc., is made to dissolve or diffuse a diamine compound and acid 2 anhydride in an organic polar solvent first, and is obtained.

[0017] especially the addition sequence of each component is not limited, but adds acid 2 anhydride previously into the organic polar solvent, adds a diamine compound, and is good also as a solution of a polyamide acid polymer —

carrying out — some diamine compounds — the inside of an organic polar solvent — previously — optimum dose, in addition a degree — acid 2 anhydride — adding — the diamine compound of the remainder [ last ] — in addition, it is good also as a solution of a polyamide acid polymer. In addition, well-known various polymerization methods are in this contractor.

[0018] As an organic polar solvent used for the generation reaction of a polyamide acid solution For example, sulfoxide system solvents, such as dimethyl sulfoxide and diethyl sulfoxid , Formamide system solvents, such as N,N-dimethylformamide, N, and N-diethyl formamide, Acetamide system solvents, such as N,N-dimethylacetamide, N, and N-diethyl acetamide, Phenol system solvents, such as pyrrolidone system solvents, such as a N-methyl-2-pyrrolidone, a phenol, o-, m- or p-cresol, KISHINORU, a halogenation phenol, and a catechol, or hexamethylphosphoramide, gamma-butyrolactone, etc. can be mentioned. Furthermore, it can also use combining aromatic hydrocarbon, such as these organic polar solvents and xylenes, or toluene, if needed.

[0019] The dehydration ring closure of the polyamide acid polymer obtained above is carried out by the thermal or chemical approach, and thermoplastic polyimide is obtained. All of the chemical approach which dehydrates using the thermal approach and dehydrating agent which heat-treat a polyamide acid solution and are dehydrated as the approach of imide-izing are used. As a dehydrating agent by the chemical approach, an aliphatic series acid anhydride and aromatic series acid anhydrides, such as an acetic anhydride, are mentioned, for example. Moreover, as a catalyst, heterocycle tertiary amine, such as aromatic series tertiary amine, such as aliphatic series tertiary amine, such as triethylamine, and dimethylaniline, a pyridine, and an isoquinoline, is mentioned. The thermoplastic polyimide obtained as mentioned above can blend an epoxy resin and a curing agent as a solution as it is, and can use them as a glue line of the adhesive covering film of this invention. Or although the solvent used for the polymerization of a polyamide acid is melted well, after throwing in a polyimide solution in the poor solvent which polyimide cannot dissolve easily, depositing polyimide resin, removing, refining and drying an unreacted monomer and considering as solid polyimide resin, it can dissolve in an organic solvent again, an epoxy resin and a curing agent can be blended, and it can also use for the glue line of the adhesive covering film of this invention. As a poor solvent to be used, an acetone, a methanol, ethanol, isopropanol, benzene, methyl cellosolve, a methyl ethyl ketone, etc. are mentioned.

[0020] As the thermal approach, after carrying out the polymerization of the polyamide acid, it supplies in vacuum oven, for example, and imide-ization is performed by heating under reduced pressure, and the technique taken out as solid polyimide resin is mentioned.

[0021] Especially limitation does not have the epoxy resin used for the adhesives of this invention. Bisphenol A mold resin, such as Epicoat 828 (oil-ized shell company make), Orthochromatic cresol novolak resin, such as 180S65 (oil-ized shell company make), Bisphenol A novolak resin, such as 157S70 (oil-ized shell company make), Tris hydroxyphenyl methane novolak resin, such as 1032H60 (oil-ized shell company make), The naphthalene aralkyl novolak resin of ESN375 grade, tetrapod FENI roll ethane 1031S (oil-ized shell company make), YGD414S (Tohto Kasei), tris hydroxyphenyl methane EPPN502H (Nippon Kayaku), Special bisphenol VG3101L (Mitsui Chemicals), the special naphthol NC 7000 (Nippon Kayaku) Glycidyl amine type resin, such as biphenyl mold epoxy NC 3000 (Nippon Kayaku), TETRAD-X, and TETRAD-C (Mitsubishi Gas Chemical Co., Inc. make), etc. is mentioned as an example of representation.

[0022] the mixed rate of an epoxy resin — the thermoplastic polyimide 100 weight section — receiving — 1 - 50 weight section — 5 - 40 weight section is preferably desirable. When many [ when too few bond strength is low, and / too ], it may be inferior to flexibility and thermal resistance.

[0023] If the curing agent is generally used as a curing agent for epoxy resins, it is good anything. A curing agent is added to adhesives for [ , such as absorptivity, thermal resistance, and an adhesive property ] improvement, and the common curing agent for [ , such as an acid 2 anhydride system, an amine system, and an imidazole system, ] epoxy, an accelerator, or various coupling agents are mentioned typically.

[0024] As mentioned above, although explanation about each presentation of the adhesives used for the adhesive covering film of this invention was given, the concentration of the adhesives solution at the time of forming a glue line is 15 - 30 % of the weight especially preferably ten to 40% of the weight preferably five to 50% of the weight in the amount of solid content (thermoplastic polyimide + epoxy resin + curing agent) which makes solution weight a denominator. Moreover, what is necessary is just to opt for the procedure of the dissolution etc. suitably in consideration of workability etc.

[0025] The adhesive covering film concerning this invention obtained as mentioned above has the property that it may be used suitable for the tape for TAB, a compound leadframe, the charge of a laminated wood, etc. On the occasion of use — since it is a thin configuration, it specifically excels in micro-processing nature, and thermal resistance and an adhesive property are excellent, and it can paste up at low temperature 200 degrees C or less — it excels in workability. When an example of the adhesion conditions in this case is given, they are about [ heating tim 5-20 minute ] conditions whenever [ stoving temperature ] in 150 degrees C - 200 degrees C and pressure 0.1-10MPa.

[0026]

[Example] O It stirred until it took dimethylformamide (it is called Following DMF) to the polyimide film reactor which does not contain the production (1) inorganic filler of a base polyimide film, it took to it 4.5Eq of ODA, and 5.5Eq of p-PDA and ODA and p-PDA dissolved in it completely. Next, 4.5Eq of TMHQ(s) was added and they were stirr d for 30 minutes after that. Then, in addition, it stirred for 120 minutes 5Eq of PMDA(s). And the solution which melt d 0.5Eq of PMDA(s) to DMF was added gradually, cooling stirring was carried out for 60 minutes, and the DMF solution

of a polyamide acid was obtained. In addition, the amount of DMF used was adjusted so that the AUW which doubled the diamine component and the acid 2 anhydride component might turn into 15% of the weight of polyamide acid organic solvent solution weight. Next, DMF, the acetic anhydride, and the isoquinoline were mixed, and the polyamide acid organic solvent solution was extruded from the die, and carried out the cast on the endless belt. Stoving was carried out until the volatile component became 50% to the film weight after baking on the endless belt, and it fixed to the pin seat which tears off the green sheet which has free-standing [ this ] from an endless belt, and conveys the both ends of a sheet continuously, and conveyed and heated to the 200,400 or 510-degree C heating furnace. Furthermore, it cooled gradually to the room temperature with the lehr. The film was torn off from the pin in the place taken out from \*\*\*\*\*. In addition, it was made for the thickness of a film to become 7.5 microns.

(2) The DMF solution of a polyamide acid was obtained like the polyimide film (1) containing an inorganic filler. In addition, the amount of DMF used was adjusted so that the AUW which doubled the diamine component and the acid 2 anhydride component might turn into 15% of the weight of polyamide acid organic solvent solution weight. Next, DMF, AA, IQ, and calcium phosphate (inorganic filler) were mixed, and the polyamide acid organic solvent solution was extruded from the die, and carried out the cast on the endless belt. Stoving was carried out until the volatile component became 50% to the film weight after baking on the endless belt, and it fixed to the pin seat which tears off the green sheet which has free-standing [ this ] from an endless belt, and conveys the both ends of a sheet continuously, and conveyed and heated to the 200,400 or 510-degree C heating furnace. Furthermore, it cooled gradually to the room temperature with the lehr. The film was torn off from the pin in the place taken out from \*\*\*\*\*. In addition, it was made for the thickness of a film to become 7.5 microns. When the transparency mold microscope estimated the obtained film, the 300 more than fine particles of magnitude (1-10micro) existed.

[0027] (Example 1) 2 and 2-screw (4-hydroxyphenyl) PUROPANJIBENZOETO -3, 3', 4, and 0.112 mols (henceforth ESDA) of 4'-tetracarboxylic dianhydride were added gradually, having added 3 and 3'-screw (amino phenoxyphenyl) sulfone (henceforth BAPS-M) 0.112mol to the glass flask with a capacity of 1000ml at dimethylformamide (henceforth DMF) 263g, and stirring under nitrogen-gas-atmosphere mind. It stirred for 30 minutes under the ice bath, stirring was stopped in the place where viscosity reached 1500poise(s), and the polyamide acid solution was obtained.

[0028] After adding DMF 113g, beta-picoline 26g, and 45g of acetic anhydrides to this polyamide acid solution and agitating for 30 minutes, it agitated for 1 hour and was made to imide-ize under 100 more degrees C. Then, this solution was hung down little by little into the methanol agitated at high speed. The mixer ground the yarn-like polyimide which deposited in the methanol, the methanol performed Soxhlet washing, it was made to dry at 110 degrees C for 2 hours, and polyimide powder was obtained. The polyimide powder obtained above was added to 20g, Epicoat 1032H60 (oil-ized shell company make) were added to 102g THF, it stirs.g [ 5 ], 4, and 4'-diamino diphenyl sulfone (curing agent) 1.5g was dissolved, and the polyimide system adhesives solution was obtained (solid-content concentration: SC=20%).

[0029] The obtained polyimide system adhesives solution was cast on the polyimide film (with no inorganic filler) of 7.5-micrometer thickness, it dried for 10 minutes at 150 degrees C after desiccation for 10 minutes by 100 degrees C, and the film-like laminating member with a thickness of 10 micrometers was obtained.

[0030] (Example 2) Fusibility thermoplasticity polyimide was obtained like the example 1 except setting an acid component to TMEG. The polyimide powder obtained above was added to 20g, Epicoat 1032H60 (oil-ized shell company make) were added to 102g THF, it stirs.g [ 5 ], 4, and 4'-diamino diphenyl sulfone (curing agent) 1.5g was dissolved, and the polyimide system adhesives solution was obtained (solid-content concentration: SC=20%).

[0031] The obtained polyimide system adhesives solution was cast on the polyimide film (with no inorganic filler) of 7.5-micrometer thickness, it dried for 10 minutes at 150 degrees C after desiccation for 10 minutes by 100 degrees C, and the film-like laminating member with a thickness of 10 micrometers was obtained.

[0032] (Example 3) Fusibility thermoplasticity polyimide was obtained like the example 1 except setting an amine component to APB. The polyimide powder obtained above was added to 20g, Epicoat 1032H60 (oil-ized shell company make) were added to 102g THF, it stirs.g [ 5 ], 4, and 4'-diamino diphenyl sulfone (curing agent) 1.5g was dissolved, and the polyimide system adhesives solution was obtained (solid-content concentration: SC=20%). The obtained polyimide system adhesives solution was cast on the polyimide film (with no inorganic filler) of 7.5-micrometer thickness, it dried for 10 minutes at 150 degrees C after desiccation for 10 minutes by 100 degrees C, and the film-like laminating member with a thickness of 10 micrometers was obtained.

(Example 4) Fusibility thermoplasticity polyimide was obtained like the example 1 except setting an acid component to TMEG and setting an amine component to APB. The polyimide powder obtained above was added to 20g, Epicoat 1032H60 (oil-ized shell company make) were added to 102g THF, it stirs.g [ 5 ], 4, and 4'-diamino diphenyl sulfone (curing agent) 1.5g was dissolved, and the polyimide system adhesives solution was obtained (solid-content concentration: SC=20%).

[0033] The obtained polyimide system adhesives solution was cast on the polyimide film (with no inorganic filler) of 7.5-micrometer thickness, it dried for 10 minutes at 150 degrees C after desiccation for 10 minutes by 100 degrees C, and the film-like laminating member with a thickness of 10 micrometers was obtained.

(Example 5) The polyimide powder obtained in the example 1 was added to 20g, TETRAD-C (Mitsubishi Gas Chemical Co., Inc. make) was added to 102g THF, it stirs.g [ 5 ], 4, and 4'-diamino diphenyl sulfone (curing agent) 1.5g was dissolved, and the polyimide system adhesives solution was obtained (solid-content concentration: SC=20%).

[0034] The obtained polyimide system adhesives solution was cast on the polyimide film (with no inorganic filler) of

7.5-micrometer thickness, it dried for 10 minutes at 150 degrees C after desiccation for 10 minutes by 100 degrees C, and the film-like laminating member with a thickness of 10 micrometers was obtained.

[0035] (Example 1 of a comparison) It cast so that it might be set to 15 micrometers after drying the polyimide system adhesives solution obtained in the example 1 on the polyimide film (APIKARU 25AH, Kaneka Co., Ltd. make) of 25-micrometer thickness, and it dried for 10 minutes at 150 degrees C after desiccation for 10 minutes by 100 degrees C, and the film-like laminating member with a thickness of 0 micrometer was obtained.

[0036] (Example 2 of a comparison) 0.112 mols (henceforth BPDA) of biphenyl tetracarboxylic dianhydride were added gradually, having added 3 and 3'-screw (amino phenoxyphenyl) sulfone (henceforth BAPS-M) 0.112mol to the glass flask with a capacity of 1000ml at dimethylformamide (henceforth DMF) 263g, and stirring under nitrogen-gas-atmosphere mind. It stirred for 30 minutes under the ice bath, stirring was stopped in the place where viscosity reached 1500poise(s), and the polyamide acid solution was obtained.

[0037] After adding DMF113g, beta-picoline 26g, and 45g of acetic anhydrides to this polyamide acid solution and agitating for 30 minutes, it agitated for 1 hour and was made to imide-ize under 100 more degrees C. Then, this solution was hung down little by little into the methanol agitated at high speed. The mixer ground the yarn-like polyimide which deposited in the methanol, the methanol performed Soxhlet washing, it was made to dry at 110 degrees C for 2 hours, and polyimide powder was obtained. The polyimide powder obtained above was not able to be dissolved in THF. (Solid-content concentration: SC=20%) .

[0038] (Example 3 of a comparison) 2 and 2-screw (4-hydroxyphenyl) PUROPANJIBENZOETO -3, 3', and 4 and 0.112 mols (henceforth ESDA) of 4'-tetracarboxylic dianhydride were added gradually, having added oxy-dianiline (henceforth ODA) 0.112mol to the glass flask with a capacity of 1000ml at dimethylformamide (henceforth DMF) 263g, and stirring under nitrogen-gas-atmosphere mind. It stirred for 30 minutes under the ice bath, stirring was stopped in the place where viscosity reached 1500poise(s), and the polyamide acid solution was obtained.

[0039] After adding DMF113g, beta-picoline 26g, and 45g of acetic anhydrides to this polyamide acid solution and agitating for 30 minutes, it agitated for 1 hour and was made to imide-ize under 100 more degrees C. Then, this solution was hung down little by little into the methanol agitated at high speed. The mixer ground the yarn-like polyimide which deposited in the methanol, the methanol performed Soxhlet washing, it was made to dry at 110 degrees C for 2 hours, and polyimide powder was obtained. The polyimide powder obtained above was not able to be dissolved in THF (solid-content concentration: SC=20%).

[0040] (Example 4 of a comparison) Fusibility thermoplasticity polyimide 20g obtained in the example 1 was dissolved in THF, and the fusibility thermoplasticity polyimide solution was obtained. The obtained solution was cast on the polyimide film (APIKARU7.5H.P., Kaneka Co., Ltd. make) of 7.5-micrometer thickness, it dried for 10 minutes at 150 degrees C after desiccation for 10 minutes by 100 degrees C, and the film-like laminating member with a thickness of 10 micrometers was obtained.

[0041] (Example 5 of a comparison) The plater bond M1276 (copolyamide, the Japanese Lil Sun Co., Inc. make) was dissolved in 10g, 20g and diamino diphenyl ape phon 1g were dissolved for Epicoat 1032H60 (oil-ized shell company make) in 83g THF, and the adhesives solution was obtained. The obtained solution was cast on the polyimide film (APIKARU7.5H.P., Kaneka Co., Ltd. make) of 7.5-micrometer thickness, it dried for 10 minutes at 150 degrees C after desiccation for 10 minutes by 100 degrees C, and the film-like laminating member with a thickness of 10 micrometers was obtained.

[0042] (Example 6 of a comparison) The polyimide system adhesives solution obtained like the example 1 was cast on the polyimide film (those with an inorganic filler) of 7.5-micrometer thickness, it dried for 10 minutes at 150 degrees C after desiccation for 10 minutes by 100 degrees C, and the film-like laminating member with a thickness of 10 micrometers was obtained.

[0043] (Characterization of a film-like laminating member)

1. Laser processing was carried out on condition that below micro-processing nature, and configuration observation was performed in SEM. The degree of a taper and the vacancy condition of a hole were evaluated in three steps. Use device: lambda= 355nm bore-diameter:40-micrometer rate:100 hole / UV individual laser (3rd higher harmonic of YAG), and sec laser oscillation:20kHzO [ Peeling strength when pasting up a laminating member and copper foil in the following procedures was measured. ] .. A taper and a hole are fitness \*\*. A hole is x in which weld flash remains although it has opened.. It is 2. peeling strength with the part into which the hole has not opened. Heating pressurization of a film-like laminating member and the 18-micrometer electrolytic copper foil was carried out for 20 minutes by the temperature of 200 degrees C, and pressure 3MPa, and the copper-clad flexible laminate was obtained. The obtained copper-clad flexible laminate lengthens, and it removes, and is JIS about reinforcement. It measured according to C6481. However, the conductor width was measured by 3mm.

3. Using the copper clad laminate obtained by heat-resistant two, lengthen 1000 hours after 150 degree-Cx, remove, and it is JIS about reinforcement. It measured according to C6481. However, the conductor width was measured by 3mm.

[0044] The characterization result of the film-like laminating member of an example and the example of a comparison is shown in Table 1.

[0045]

[Table 1]



	レーザー加工性	接 強度	
		常態	150°C×1000時間
実施例 1	○	9	7
実施例 2	○	10	6
実施例 3	○	9	7
実施例 4	○	11	6
実施例 5	○	10	7
比較例 1	×	9	7
比較例 2	—	—	—
比較例 3	—	—	—
比較例 4	○	1	1
比較例 5	○	9	2
比較例 6	×	9	7

[0046]

[Effect of the Invention] The adhesive covering film of this invention has the configuration which carried out the laminating of the 10 micrometers or less of the 0.5–5-micrometer glue lines to the high elasticity ultra-thin polyimide film which does not contain an inorganic filler with a thickness of 3–7.5 micrometers preferably, and micro-processing nature which is not in the former can be realized by setting the total thickness to 10 micrometers or less. Moreover, it can have electric dependability, the outstanding adhesive property, and outstanding thermal resistance by constituting a glue line from fusibility thermoplasticity polyimide resin, an epoxy resin, and its curing agent.

[Translation done.]